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Curvature Dependent Reactivity of Fullerenes and Nanotubes

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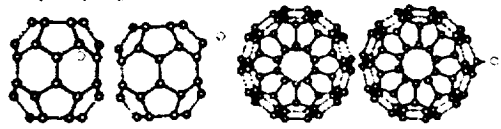
Curvature Dependent Reactivity

- Example: Hydrogenation of Fullerenes and Nanotubes



-1.54 eV -4.50 eV -1.23 eV -3.18 eV

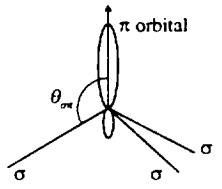
- External Surface : Nucleophilic
  Internal Surface : Electrophilic
- Chemical reactivity is a function of the curvature of fullerene.

Depedence on PyramidalizationAngle ?

- The Chemical Reactivity of Fullerene ⟵ The pyramidalization.
- Pyramidalization ⟶ Between sp^2 and sp^3
- Between sp^2 and sp^3

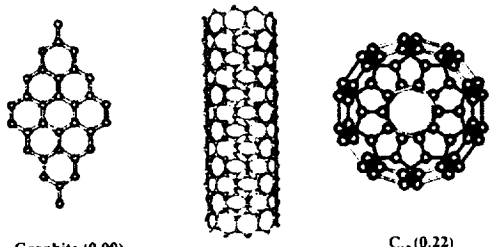
Less Energy needed than sp^2

sp^3



- Pyramidal angle (θ_p) = θ_{ort} - $\pi/2$

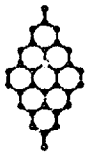
Three Examples of Surfaces



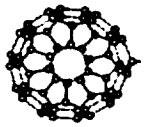
Graphite (0.00) (10,0) Nanotube (0.09) C_{60} (0.22)

Example: Reaction on Surfaces

- Hydrogenation of graphene sheet and Fullerenes



H on Graphite
E = –4.50 eV
θ_p = 12.95° (0.226)
θ_s = 0.0° (0.0)

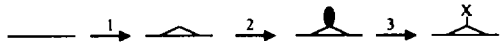


H on C_{60}
E = –3.18 eV
θ_p = 20.56° (0.359)
θ_s = ? (0.22)

- Chemical reactivity difference ≠ Strain energy difference ?

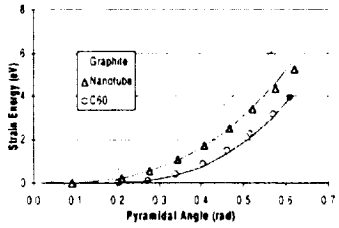
External Chemical Reaction on Fullerene

- Total reaction energy
  1. Straining the bonds. (+ΔE)] Strain Energy
  2. Breaking π bonds. (+ ΔE)] Binding Energy
  3. Reacting with external reactant (X) in given structure. (- ΔE)
  4. Global relaxations (- ΔE) ← Temporally ignored



Strain Energy Contribution to Reaction

- Fix all the carbon atoms, pull only one carbon up and calculate the energy difference



1. Elastic Strain Energy
2. Independent of External Reactant
3. θ_0 shift
4. θ_0 increase ⇒ stiffer

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- The relation with the pyramidal angle (θ_p)

$$|\pi\rangle = \sqrt{2}\tan(\theta_p)|s\rangle + \sqrt{1-2\tan^2(\theta_p)}|p\rangle$$

- Binding energy with external reactant *X*

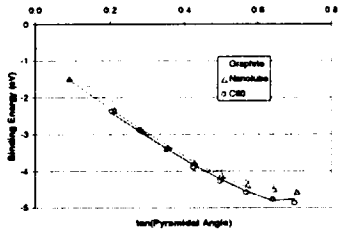
$$E_{binding} = \sqrt{2}\tan(\theta_p)\,E_{sx} + \sqrt{1-2\tan^2(\theta_p)}\,E_{px} + E_{\pi\ breaking}(\theta_0)$$

where $E_{sx} = \langle X|H|s\rangle$ and $E_{px} = \langle X|H|p\rangle$

- E_{sx} and E_{px} depends only on external reactant *X*.

Binding Energy Dependence on Pyramidal Angle

- Hydrogen is used as the point probe.



1. E_{sc} = -5.34 eV
   E_{ss} = -1.71 eV
2. $\Delta E_{\pi\ breaking}$
   -0.1 eV ~ -0.3 eV
3. Independent of θ_0
4. Almost linear in small θ_p

Total Reaction Energy Estimation

- Total reaction energy = Minimum (strain energy + binding energy)
- Small Errors (~ 0.1 eV) from ignoring global relaxation

Formation Energy Comparison with Full Relaxation Results

	Pyramidal Angle (θ_p)			Total Reaction Energy (eV)	
	Initial Value	Estimated Value	Full Relaxation	Estimated Value	Full Relaxation
Graphite	0.000	0.220	0.226	-1.50	-1.63
Nanotube	0.091	0.291	0.292[a]	-2.29	-2.39
C_{60}	0.202	0.373	0.359	-3.07	-3.18

a) The forces are relaxed up to the first nearest neighbors

External Chemical Reactivity (Conclusions?)

- θ_0 (initial pyramidal angle) { Strain Energy curve shift θ_0 / Binding Energy curve shift < ~ 0.3 eV
- Binding Energy curve ~ almost linear
  $\theta_p = \theta_C + \theta_0 - \delta$ (stiffness change)
- Total reaction energy changing by θ_0
  Strain energy effect < 0.1 eV
  Binding energy effect ~ $\theta_0 E_{sc}$ eV

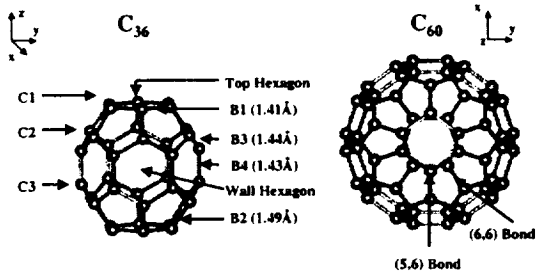
Internal Reaction

- Less Reactive than External Reaction ← Less Electron Density
- Total reaction energy
  1. Straining the bonds. (+ ΔE)
  2. Breaking π bonds. (+ ΔE)
  3. Reacting with external reactant (X) in given structure. (- ΔE)
  4. Global relaxations (- ΔE)

  } Same as External Chemical Reaction

  5. Weak bonds with neighbor carbon atoms. (- ΔE) → Difference from External Reaction

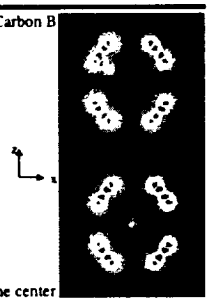
C_{36} and C_{60}



H @ C_{36} and H @ C_{60}

		Initial θ_p	Final θ_p	Formation Energy
C_{36}	C1	72.85	75.21	-1.28
	C2	73.95	77.87	-1.54
	C3	77.19	81.53	-1.40
	Center			-0.46
C_{60}	Carbon	78.37	85.35	-1.23
	Center			-0.43

H on Carbon B

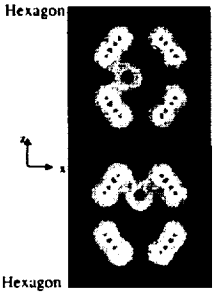


H at the center

P @ C_{36} and P @ C_{60}

		Formation Energy
C_{36}	Top Hexagon	-0.27
	Pentagon	-0.74
	Wall Hexagon	-0.89
	Bond 4	-0.80
	Carbon 3	-0.85
C_{60}	(6,6) Bond	-0.81
	Center	-0.99

Wall Hexagon



Top Hexagon

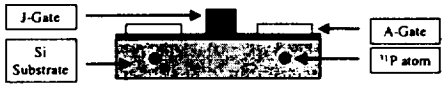
- The other sites are unstable.

Internal Chemical Reactivity

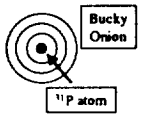
- As θ_p increases
  - The portion of π state decreases (+ ΔE)
  - π bond breaking energy decreases (- ΔE)
  - Global Interaction increases (- ΔE)
- Two negative effect and one positive effect combined.
  - ⟶ Hard to estimate reaction energy

Quantum Computer

- Solid state quantum computer can be designed by ^{31}P atoms in bulk Si [1].

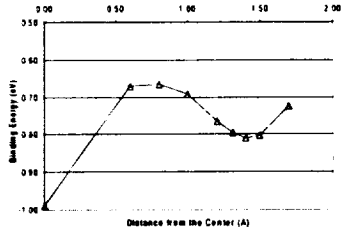


- Remaining Problems
  - Placing of a ^{31}P atom
  - Diffusion of a ^{31}P atom
  - ^{31}P @ Bucky Onion
- ^{31}P @ Bucky Onion
  - Possible self-ordering
  - Preventing diffusion of ^{31}P



1. Kane, B.E., *Nature*, 393, p.133 (1998)

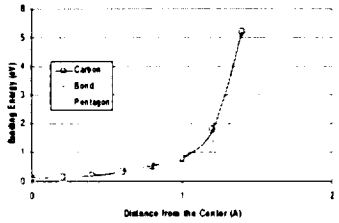
P @ the Center of C_{60}

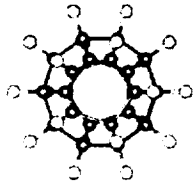


- Full Relaxation
- Binding Energy
  Center : -0.99 eV
  (6,6) Bond : -0.81 eV
- Diffusion Barrier
  Center ⇒ Bond
  -0.33 eV

H @ $C_{20}D_{20}$

- No meta-stable site and Diffusion Barrier = 1.17 eV





$C_{20}D_{20}$

Conclusions

- The external reaction energy is determined by a competition of strain energy and binding energy.
- We can estimate external reaction energy up to 0.1 eV error, which is from global relaxation.
- External Chemical Reactivity is enhanced by binding energy difference due to initial pyramidal angle.
- Inner Chemical Reactivity is enhanced by Global Interactions.
- Possible candidates for Quantum Computer
  ^{31}P @ C_{60} and ^{1}H @ $C_{20}D_{20}$

Future Work

- We are going to test more examples on external chemical reactivity.
- We will continue to work on the reactivity of the multi-bonds reactions and non-covalent bond reactions.
- We need more systematic study on internal chemical reactivity.
- Since we found the way to encapsulate P and H, we will work on self-ordering of endo-fullerene for quantum computer application.
- As an another candidate for quantum computer, we are looking into compressed bucky onion, which has diamond core structure.

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